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PROPERTIES OF REACTIVE SPECIES GENERATED AT HIGH
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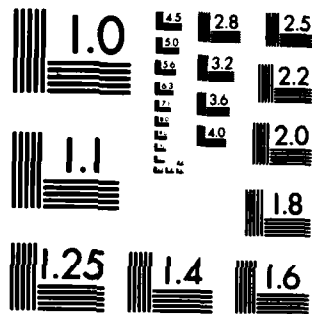
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Reactions of iron, cobalt, nickel, palladium and zirconium atoms with unsaturated hydrocarbons are described. Preliminary studies of a number of other atoms are described: Th, Rh, Nb, Ta.		

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AFOSR-TR- 83 - 0240

FINAL SCIENTIFIC REPORT

U.S. AIR FORCE OF SCIENTIFIC RESEARCH

Grant No.

AFOSR-79-0063

PROPERTIES OF REACTIVE SPECIES GENERATED
AT HIGH TEMPERATURES AND THEIR LOW
TEMPERATURE REACTIONS TO FORM NOVEL SUBSTANCES

Submitted by:

P. S. Skell

Principal Investigator

Davey Laboratory

The Pennsylvania State University

University Park, PA 16802

March 9, 1983

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PROPERTIES OF REACTIVE SPECIES GENERATED
AT HIGH TEMPERATURES AND THEIR LOW
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A Summary of Progress

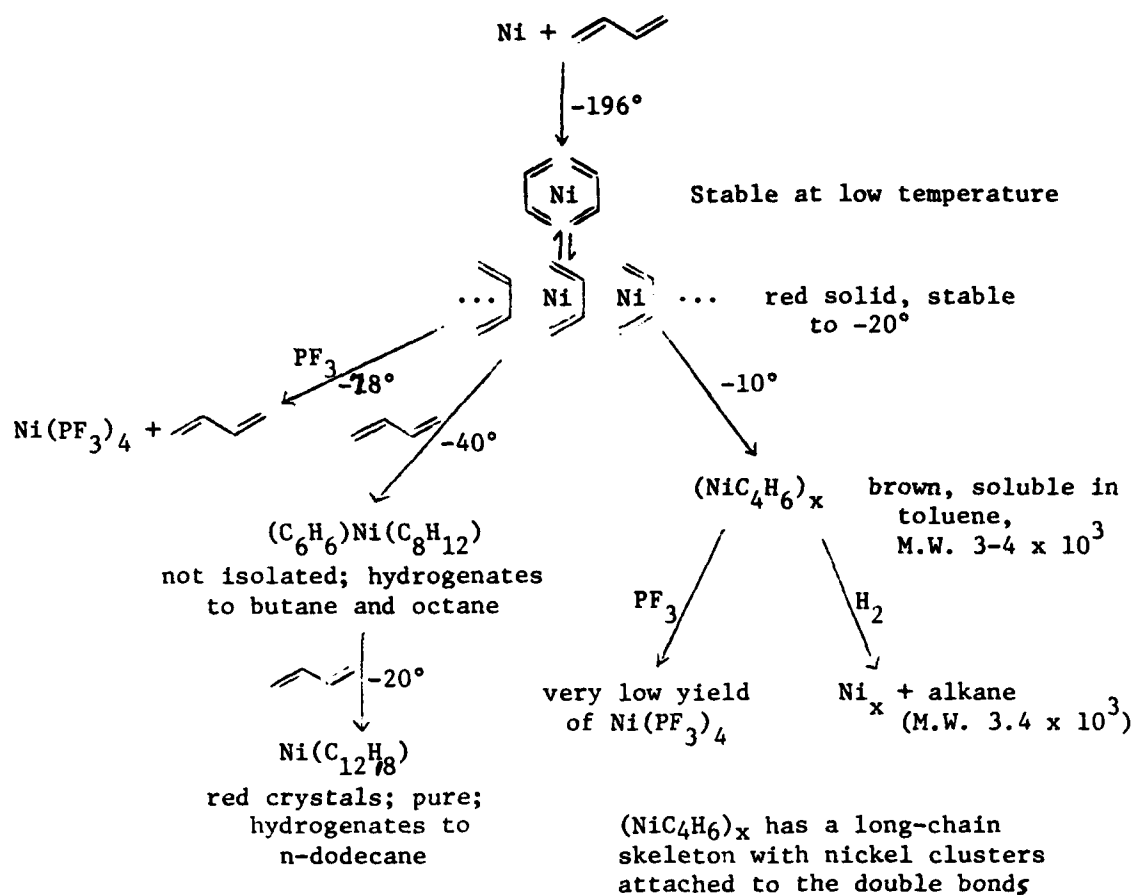
Nickel. Reactions of nickel atoms with 1,3-dienes has been the most extensively studied, both by isolation of products and by matrix spectroscopy. Scheme I summarizes the results for 1,3-butadiene; there are quantitative, but not qualitative differences with isoprene, piperylene, and 2,3-dimethylbutadiene; 1,3-cyclohexadiene is qualitatively different since it undergoes disproportionation.

With isoprene alone a new type of product is obtained in 10% yield, a volatile, extremely stable, purple compound, $C_{10}H_{14}Ni$. There are two isomers present, one of which is fully characterized in Scheme II. With the completion of analogous work on the other isomer, this program should be near to a conclusion.

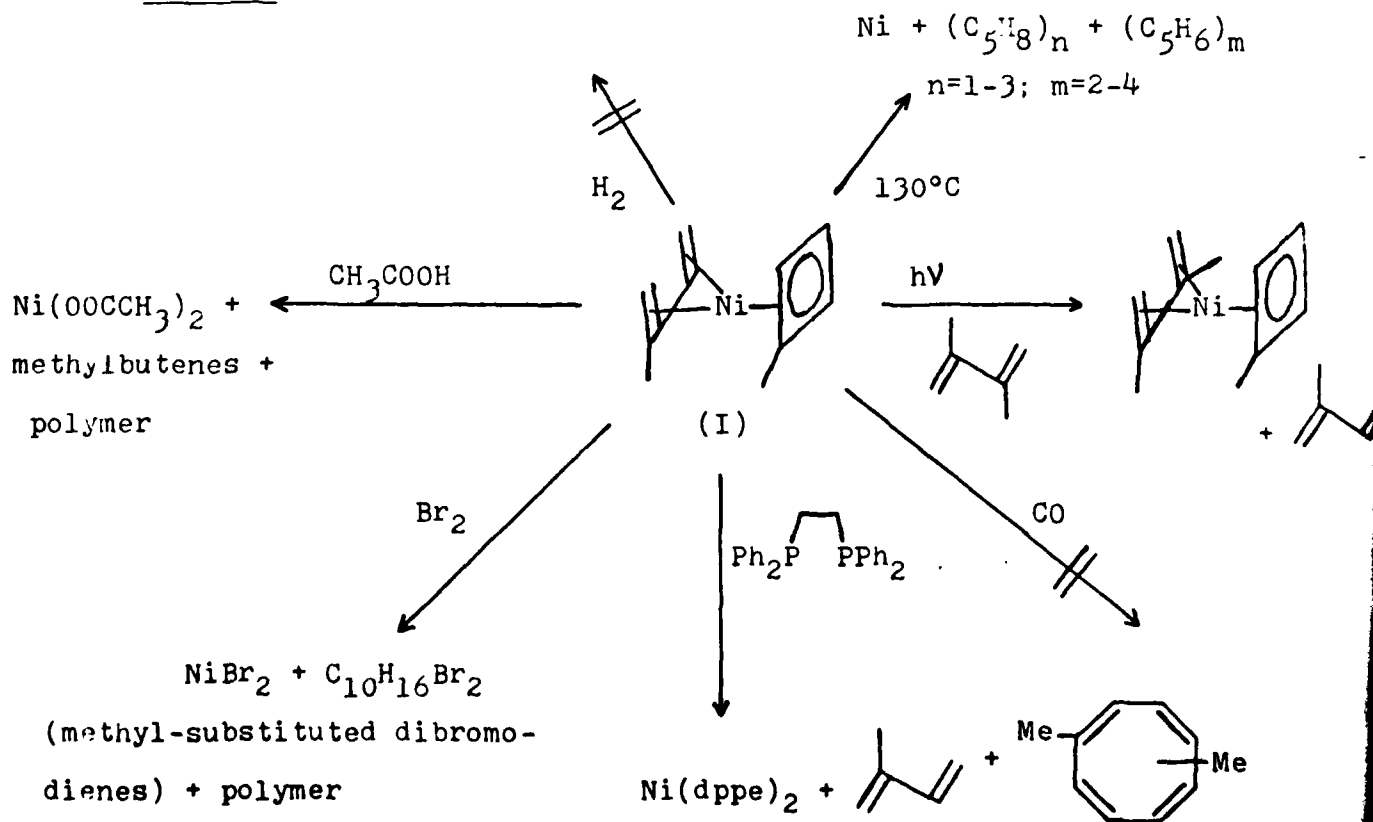
Cobalt. The most intriguing aspect of this investigation is the preparation of an olefin isomerization catalyst with minimum turnovers per hour at -78° of 600, and an olefin hydrogenation catalyst with turnovers per hour at -78° of 15-30. Unfortunately these catalysts have not

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Scheme II



been isolated and so far one cannot specify structures. The turnovers are per mole Co. The evidence indicates the catalysts are more than mononuclear, making the turnovers per mole of catalyst larger by the multiplying factor of the nuclearity.

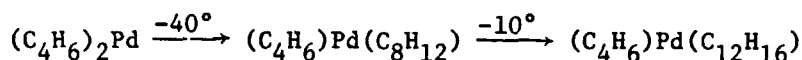
The catalysts are prepared by making the soluble toluene complex with the reaction of toluene and cobalt atoms. Addition of 1-butene to this solution (-78°) results in a slow steady isomerization (6 turnovers per hour) to pure trans-2-butene (equilibrium mixture contains 12% cis-2-butene). Addition of hydrogen to this reaction system results in an immediate increase of rate to values as high as 600 turnovers per hour, but the catalyst life is now very short. Although isomerization comes to a halt, the resulting solution contains a long-lived olefin hydrogenation catalyst with rates of 15-30 turnovers per hour at -78° , the rate dependent on the olefin structure; 1,3-butadiene is converted totally to the butenes before the butenes are hydrogenated to butane.

A range of techniques have been applied to extract structural information, but no hypothesis is satisfactory. Experiments currently in progress may lead to elucidation and thus the completion of this work.

Iron. The iron-toluene complex is stable to -50° , and is a valuable reagent for preparation of low-valent organoiron compounds. The structure of this complex is controversial. Mössbauer spectroscopy appears to provide the key to structural definition of the arene-iron atom systems. Hexamethylbenzene-iron(0), prepared by wet-methods or by atom reactions are identical; the structure has been demonstrated

to be a symmetrical sandwich. The benzene and iron atom product has the same structure. Toluene, mesitylene and t-butylbenzene products are mixtures of similar amounts of two compounds: 1) an iron (0) complex similar to hexamethylbenzene and benzene sandwiches, and 2) a complex with splittings characteristic of iron(2). This work will draw to a close with the characterization of the iron(2) compounds.

Palladium. These atoms undergo reactions with 1,3-dienes similar to those of nickel, making a bis-1,3-dienepalladium complex, stable at -78° . Warming in the presence of excess diene produces successively (illustrated for butadiene) two products.



In two respects the palladium system differs from the nickel system:

- 1) palladium 2:1 complex cannot be converted to the 1:1 complex, and
- 2) on warming the complex in the absence of excess diene only palladium metal and unpolymerized diene are obtained. With 2,3-dimethylbutadiene, the oligomerized substances are not produced, only the $(\text{C}_6\text{H}_{10})_2\text{Pd}$; this complex decomposes to diene and metal on warming to 0° .

Molybdenum. A series of bis-arene complexes has been prepared by the atom method, including the mixed complexes. The arene substituents range: CO_2CH_3 , CF_2 , F, H, alkyl, $(\text{CH}_3)_2\text{N}$, OCH_3 . Relative rates of formation were examined by competition methods and they were found to be spread over less than a factor of 3 for both the first and second steps of formation of the bis-arenemolybdenums at -196° .

A series of compounds have been made from reactions of Mo atoms

with mixtures of cyclopentadiene and arenes, resulting in $(C_5H_5)Mo(C_6H_5X)$ and $(C_5H_5)Mo(H)(C_6H_5X)$, the former with $X = COOCH_3$, the latter with $X = (CH_3)_2N$ and other substituents. An X-ray structure of the carbomethoxy derivative is near completion. When the interconversion of the 17e and 18e compounds are understood, this work will be complete.

Molybdenum (and tungsten atoms) catalyze at -20° the rapid metathesis-polymerization of norbornene and norbornadiene.

Zirconium. A complex, stable at low temperatures, is made from reactions of zirconium atoms and toluene. This complex reacts with cyclooctatetraene to make $(C_7H_8)Zr(C_8H_8)$. With pentamethylcyclopentadiene, zirconium makes the bis-cyclopentadienylcyclopentadienezirconium. The most remarkable property of zirconium atoms is the ability to react with alkanes, inserting into C-H and C-C bonds, making four bonds per zirconium to the alkane fragments.

These experiments were done with small amounts of metal atom, obtained by vaporization from a tungsten wire coated with powdered zirconium. The elucidation of the detailed structure of the products from alkanes and zirconium atoms, and the further exploration of zirconium atom reactions is one of the major new activities for this proposal. The new e-gun vaporization methods have overcome the difficulties in the earlier work.

Thorium. Preliminary experiments with thorium atoms vaporized from tungsten wire coated with thorium powder indicate a close similarity to zirconium atom chemistry.

Rhodium. This metal can be vaporized in small amounts from a tungsten wire

on which rhodium metal is electroplated. Preliminary reactions with alkenes and arenes gives products which appear to be π -complexes.

With e-gun vaporization this work will become a major activity.

Atom Potential. The name is a derivative from "metal potential" and is a potential for the process: atom \rightarrow solvated ion + electrons. An atom potential table has been elaborated for most of the metal atoms; it is quite different from the familiar Standard Potentials. The atom potential table correlates the reactivities of the atoms in liberating H_2 from water and methanol at -196° , and the reduction of acetone. We anticipate this table will correlate the electron-transfer properties of the metal atoms.

Published Atom Work for the High Boiling Metals

Boron. No publications other than references in review articles to W. Brent's PSU thesis, work done with magnetically-focussed e-gun, with the attendant substrate damage.

Cerium. C. W. DeKock and coworkers obtained $Ce_2(COT)_3$ from reaction of Ce atoms with COT.¹

¹C. W. DeKock, S. R. Ely, T. E. Hopkins, and M. A. Brault. Inorg. Chem., 17, 625 (1978).

Hafnium. Two communications by M. L. H. Green and coworkers,^{2,3} one reporting the isolation of $(arene)_2Hf(PMe_3)$ and $(C_7H_7)Hf(C_7H_9)$ from reactions of the metal atoms with benzene or toluene and PMe_3 for the former, and cycloheptatriene for the latter.

²F. G. N. Cloke and M. L. H. Green, J. Chem. Soc. Chem. Commun., 127 (1979).

³T. G. N. Cloke, M. L. H. Green, and P. J. Lennon, J. Organometal. Chem., 188, C25 (1980).

Iridium. No publications.

Molybdenum. Work done at PSU with vaporization of resistively heated molybdenum wire (a highly satisfactory method). Published work includes the synthesis of numerous (arene)₂Mo,⁴ Cp₂MoH₂, (C₇H₇)Mo(C₇H₉) (from cycloheptatriene), (C₇H₇)Mo(C₅H₅)⁵ (from cycloheptatriene and cyclopentadiene), tris-butadienemolybdenum (including its crystal structure).⁶ See also work reported in the preceding section of this proposal. D'Anniello and Barefield also reported the synthesis of Cp₂MoH₂.⁷ Green and co-workers reported the reaction of DMPE with Mo atoms to produce Mo(DMPE)₃.⁸

⁴P. S. Skell, M. P. Silvon, and E. M. Van Dam, J. Am. Chem. Soc., 96, 1945 (1974).

⁵E. M. Van Dam, W. N. Brent, M. P. Silvon, and P. S. Skell, J. Am. Chem. Soc., 97, 465 (1975).

⁶P. S. Skell and M. T. McGlinchey, Angew. Chem. Internat. Edit., 14, 195, (1975).

⁷M. T. D'Anniello and E. K. Barefield, J. Organomet. Chem., 76, C50 (1974).

⁸F. G. N. Cloke, P. J. Fyne, M. L. H. Green, and M. J. Ledoux, J. Organomet. Chem., 198, C69 (1980).

Niobium. M. L. H. Green communications reporting the reaction of niobium atoms with 1) benzene, toluene and mesitylene do make (arene)₂Nb,⁹ and 2) DMPE to make Nb(DMPE)₃.⁸

⁹F. G. N. Cloke, M. L. H. Green, and D. H. Price, J. Chem. Soc. Chem. Commun., 431 (1978).

Osmium. No publications.

Platinum. PSU work done with resistive heating of platinum on tungsten wire, with vaporizations of only 50-75 mg of Pt atoms per run. These

experiments were used to demonstrate the synthesis, from Pt atoms, of $(1,5\text{-COD})_2\text{Pt}$, $(\text{allyl PtCl})_2$, and a π -complex of Pt and propene.

Rhenium. No publications.

Rhodium. No publications.

Ruthenium. P. L. Timms and R. B. King¹⁰ communication reporting the preparation of $(\text{C}_6\text{H}_6)_2\text{Ru}$ atoms and benzene.

¹⁰P. L. Timms and R. B. King, J. Chem. Soc. Chem. Commun., 898 (1978).

Silicon. Owens and Skell reported insertion reactions of Si atoms into alcohols and into Si-H bonds, making $(\text{RO})_2\text{SiH}_2$ and $\text{Me}_3\text{SiSiH}_2\text{SiMe}_3$ (from Me_3SiH).¹¹ This work was done with magnetic focussed e-gun, and consequent electron damage to substrates.¹²

¹¹P. W. Owen and P. S. Skell, Tetrahedron Lett., no. 18, 1807 (1972).

¹²P. S. Skell and P. W. Owen, J. Am Chem. Soc., 94, 5434 (1972).

Tantalum. Communication from M. L. H. Green and co-workers describing the reaction of Ta atoms with DMPE to make $\text{Ta}(\text{DMPE})_3$.⁸

Thorium. No publications. See earlier section of this proposal.

Titanium. Synthesis of $(\text{arene})_2\text{Ti}$ from titanium atoms and benzene, toluene or mesitylene, reported by M. L. H. Green and co-workers.¹³ These compounds were used as butadiene polymerization catalysts. PSU work with bis-toluenetitanium reported the reaction with cyclooctatetraene to make $(\text{COT})_2\text{Ti}$ and $(\text{COT})_3\text{Ti}_2$.¹⁴ P. L. Timms and T. W. Turney reported the reaction of Ti atoms with cycloheptatriene produces $(\text{C}_7\text{H}_7)\text{Ti}(\text{C}_7\text{H}_9)$.¹⁵

¹³M. T. Anthony, M. L. H. Green and D. Young, J. Chem. Soc. Dalton Trans., 1419 (1975).

¹⁴S. P. Kolesnikov, J. E. Dobson, and P. S. Skell, J. Am. Chem. Soc., 100, 999, (1978).

¹⁵P. L. Timms and T. W. Turney, J. Chem. Soc. Dalton Trans., 2021 (1976).

Uranium. Graves, Lagowski and Simons mention that U atoms react with COT to make $(COT)_2U$.¹⁶

¹⁶V. Graves, J. J. Lagowski and L. H. Simons, Chem. Eng. News., 26 (Dec. 20, 1973).

Vanadium. Fluorosubstituted bisarene vanadium complexes have been reported by K. J. Klabunde and co-workers.¹⁷ $V(\eta^6-C_7H_8)_2$ has been prepared by P. L. Timms and co-worker¹⁵ from cycloheptatriene. Very recently, M. L. H. Green and co-workers have reported the preparation of $V(DPME)_3$ from the condensation of vanadium atoms with DMPE.⁸

¹⁷K. J. Klabunde and H. F. Efner, Inorg. Chem., 14, 789 (1975).

Tungsten. P. S. Skell and co-workers have co-condensed a variety of arenes,⁴ 1,3-butadiene,⁶ cycloheptatriene, and cyclopentadiene⁵ with tungsten evaporated from a tungsten filament to give bis-arene tungsten, tris-1,3-butadiene tungsten, $(C_7H_7)W(C_7H_9)$ and $(C_5H_5)_2WH_2$, respectively. The reaction of tungsten with arene/ C_5H_6 mixtures gave a mixture of $(arene)_2W$, $areneW(C_5H_5)H$ and $(C_5H_5)WH_2$.⁵ The bis-arene-tungsten compounds were also reported by M. L. H. Green and co-workers.¹³

Zirconium. M. L. H. Green and co-workers reported the preparation of $(arene)_2Zr(PMe_3)_2$ and $(C_7H_7)Zr(C_7H_9)_3$ from the co-condensation of Zr atoms with arene/ PMe_3 mixture, and C_7H_8 , respectively. See the preceeding section of this proposal (p.5) for a description of some

of the PSU work.¹⁸

¹⁸R. J. Remick, T. Asunta and P. S. Skell, J. Am. Chem. Soc.,
101, 1320 (1979).

PSU Preliminary Exploratory Experiments

During the last year at the Pennsylvania State University, we have built two reversed-polarity electrostatically-focussed electron-gun metal atom reactors. The water-cooled hearths are maintained at positive potentials of 7-10 k volts, the filament at ground potential. By using this equipment, we can evaporate all the refractory metals in large quantity. The overwhelming stray electron problem that accompanied the using of commercially available e-guns as heating source for the metal atom syntheses has been overcome. In our new apparatus the products show no signs of electron damage.

In order to test the feasibility of this equipment for metal atom syntheses with the refractory metals, the following preliminary reactions have been carried out.

Niobium. The reactions of Nb atom with cycloheptatriene and cyclopentadiene produce $(C_7H_8)_2Nb$ and $(C_5H_5)_4Nb$, respectively. The reaction of Nb with 1,3-dienes produce dark red products.

Tantalum. The reaction of Ta atoms with cycloheptatriene produces a dark red product. The reaction of Ta atoms with cyclopentadiene produces $(C_5H_5)_4Ta$.

Tungsten. The reaction of W atoms with $C_6H_5CF_3$ produces the dark brown very stable $(C_6H_5CF_3)_2W$.

Zirconium. The reaction of Zr atoms with some 1,3-dienes (e.g., 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene) produce dark red products. A variety of arene, with different substituents have been reacted with Zr atoms in order to find the substituent effects (CO_2CH_3 , CH_3 , F, H, CH_3 , t-Bu, NMe_2) on the stability of the resulting bis-arene zirconium complexes; none are stable at room temperature; the dimethylamino derivative is the most stable.

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